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Process for dry-recycling of (U,Pu)O_2 mixed-oxide nuclear fuel scrap

The present invention relates to a process for dry recycling of (U,Pu)O_2 mixed-oxide nuclear fuel scraps.

The manufacture of fuel for light water reactors, based on uranium and plutonium oxide, generally called MOX fuel, has been the subject of various developments connected to the desire to recycle plutonium recovered during the reprocessing of spent fuel.

The manufacture and the irradiation of MOX fuel in light water reactors are now considered as a solution for giving acceptable resistance to the proliferation of plutonium separated from fission products, whether the plutonium is of civil or military origin.

Many processes for manufacturing MOX fuel have been developed during the last two decades, some calling for the complete milling of UO_2 and of PuO_2 powders in order to provide an intimate mixture, others being limited to milling only a fraction of these powders.

The MIMAS (MIcronization and MASter blend) process, which was developed by the applicant of the present invention (see figure 1), carries out the micronization by milling only a fraction of the final blend and uses two successive blending operations to allow isotopic homogenization and to take advantage of the use of free-flowing UO_2 feed products. The use of free-flowing UO_2 in the second blend and the limitation of milling to the first blend alone simplify the manufacture (for example by avoiding prior compacting/granulation or spheroidizing operations on the mixed oxide blend) and have considerably simplified qualification of the MOX fuel by users and licensing by the nuclear safety authorities, at the start of its industrialization (by virtue of the similarity in behavior of this MOX fuel and of the UO_2 fuel).

While the mixed oxide fuel is being manufactured for light water reactors, large

quantities of scraps are produced during development of the manufacturing process and continue to be produced during routine manufacture; these quantities of scrap are connected to the process itself, to the fuel user specifications, to the traceability of the products (batch production) and to monitoring their quality by sampling.

Processes for treatment of mixed oxide scraps by liquid routes are known. These processes have various considerable drawbacks: on the one hand, they generate considerable liquid effluents and additional criticality risks; on the other hand, they require additional packaging and transport in the frequent case where the liquid route treatment plant is not located on the same site as that of scrap production.

There is therefore a need to be able to directly dry-recycle manufacturing scraps of this type, at the location of their production, in the manufactured fuel.

In addition, experience has shown that dry recycling of scraps without particular precautions can lead to product defects during pellet manufacture, namely excessive variability of the physical characteristics of the product, differential-shrinkage defects (for example connected to the direct recycling of the grinding powders), blister defects caused by volatile impurities, etc. Generally, the production of a product with controlled specifications involves controlling the characteristics of the input products.

In order to solve the drawbacks mentioned above, the recycling process of the invention comprises:

- a process for manufacturing $(U,PU)O_2$ mixed oxide fuel pellets including:
    * a dispensing and a first blending of scraps in powder form and, if required, of PuO_2 and/or UO_2 powders,
    * micronization and forced sieving of said first blend,
    * another dispensing and a second blending of the first sieved blend, of UO_2 powders and, if required, of scraps in powder form,
    * pelletizing of the second blend, and
    * sintering of the resulting pellets, and
- a process for pretreating scrap including:
    * pelletizing and sintering of powder scraps in order to form scrap pellets, and
    * micronization of the scrap pellets in order to form scrap powder

designed to be incorporated as scraps in powder form into the first and/or second blends.

In this way, a process for dry-recycling the manufacturing scraps in the MOX fuel is obtained, and this process can deal with the integral quantity of scraps. This process can also be used to recycle $(U,Pu)O_2$ mixed oxide fuel scrapped due to shortage or discontinuation of its utilization.

According to one embodiment of the invention, scrap unsintered powders (for example, end-of-batch powders from pelletizing) and/or powders arising from grinding of fuel pellets are taken as powder scraps for the aforementioned pelletizing and sintering pretreatment.

According to one advantageous embodiment of the invention, up to 40% by mass of scrap, with respect to the net production of pellets, is incorporated into the aforementioned process for manufacturing fuel pellets.

Other details and particular features of the invention will emerge from the appended claims and the description of the process of the invention, given below by way of nonlimiting example, with reference to the appended drawings.

Figure 1 shows schematically the steps in the manufacture of mixed oxide fuel, according to the MIMAS process.

Figure 2 shows schematically the steps of manufacturing mixed oxide fuel and those of dry recycling, according to the invention.

In the various figures, the same references denote the same or similar elements.

In order to prevent the aforementioned drawbacks, the process of the invention for dry recycling of $(U,Pu)O_2$ mixed oxide scraps is based on a process for manufacturing $(U,Pu)O_2$ mixed oxide fuel pellets, that is to say generally (figures 1 and 2):

- a dispensing and a first blending (step 1) of scraps in powder form and, if required, of PuO_2 and/or UO_2 powders,
- micronization (step 2) of this first blend, in particular by milling, and forced

sieving (step 3) of its product, for example through a 250 µm mesh, sieve,

- another dispensing and a second blending (step 4) of the first sieved mixture, of UO_2 powders and, if required, of scrap in powder form,
- homogenization (step 5) of the second blend and addition of lubricants and/or porosity control agent(s),
- compression (step 6) of the second blend into pellets using presses (pelletizing) and
- sintering (step 7) of the resulting pellets, preferably under a wet argon and hydrogen atmosphere.

This process of manufacturing mixed oxide fuel pellets can ordinarily further comprise, for the pellets thus obtained, steps of

- dry grinding (step 8),
- sorting for aspect (step 9),
- stacking to length (step 10),
- loading the pellets into the cladding and welding the cladding in the constitution of fuel rods (step 11),
- pressurizing the rods,
- nondestructive examination of the rods (step 12), and
- assembly of the rods (step 13).

According to the invention, said recycling process comprises, in addition, a scrap pretreatment process, comprising, amongst others, steps

- of pelletizing (step 20) and of sintering (step 21) powder scraps, arising in particular from the aforementioned manufacturing process of mixed oxide fuel pellets, in order to form scrap pellets, and
- of micronization (step 23) of the scrap pellets in order to form scrap powder intended to be incorporated as scrap in powder form in the first and/or second blends (in steps 1 and/or 4).

It will be noted that the recycling process described above does not comprise (a) prior compression/granulation (or spheroidizing) step(s) usually intended to improve the flowability of the final blend and to promote filling of the matrices at the pelletizing press. The reason for this is that such steps are superfluous for the invention, because of the choice of steps for the process of the invention and because of the order in

which they occur for the products which are subjected to it.

Some parameters, which are not limiting, of the above pellet manufacturing process are given below by way of example:

- working in batches and by campaign rather than continuously,
- plutonium content of the first blend: 20 to 40%,
- milling in 60 kg quantities for an actual minimum time of 5 hours,
- use of UO_2 powders originating from ADU or AUC (known to the person skilled in the art),
- addition of 0.2 to 0.5% zinc stearate and of 0 to 1% AZB pore-forming agent (known to the person skilled in the art),
- compression by a pressure between 400 and 600 MPa,
- sintering for a minimum of 4 hours at 1650 - 1760°C in an argon environment with 5% hydrogen and an H_2/H_2O ratio of 20 to 30,
- dry centerless grinding.

During these manufacturing operations, scraps can be produced, in the process of the manufacture itself, of up to 10 to 20% of the net production, this range depending on a few important variables such as a particular specification by the user of the process or by his client (visual defect specification, for example), the size of the manufacturing campaigns, etc.

To reduce the time taken by the micronization of the scrap pellets, the process may, in addition, comprise precrushing (step 22) thereof.

It is possible to use, in a nonlimiting manner, scrapped unsintered powders and/or powders arising from grinding (step 8) of fuel pellets as powder scrap for the aforementioned pelletizing and sintering (steps 20 and 21) of the pretreatment process.

With a view to limiting the investment in plant and in premises, it is possible to use the aforementioned common fuel-pellet manufacturing equipment, that is mills, compression presses, sintering furnaces, etc. for the scrap dry-preparation steps (steps 20 to 23), with a view to recycling. The adjustment parameters for the recycling may be identical or different to those of the actual manufacture of fuel pellets. Proceeding with the process in batches and campaigns makes it possible to insert the

recycling operations between actual pellet manufacturing operations.

With regard to scrap dust and PuO_2 and UO_2 oxide dust produced during the process or transfer operations, it is possible to recover them by means of cleanable filters so as to recycle them into scrap pellets at the pelletizing and sintering steps (steps 20 and 21).

Advantageously, it is possible to incorporate up to 40% of pretreated scraps (in steps 20 to 23), with respect to the net production of fuel pellets, into the aforementioned manufacturing process thereof.

Experience has shown the applicant that it is possible to recycle, in balance with the actual manufacture, scrap produced in the manufacture, up to a percentage of 20 to 25% of the net production of these pellets.

In particular, a proportion of 99.5%, expressed as mass of PuO_2, of the scraps from the aforementioned process for manufacturing fuel pellets is dry-recycled.

The ability of the process of the invention to recycle large proportions of scrap can therefore be turned to advantage in order to recycle unusual proportions of scrap encountered, inter alia, during qualification tests of the process, during production incidents, etc.

It is possible to incorporate into said first mixture up to 100% of scrap pretreated according to the invention, whether the scrap comes from the reference MOX pellet manufacturing process (MIMAS process) or from another process.

Preferably, a ball mill is used for the micronization of the aforementioned first blend (step 2) and/or of said scrap pellets (step 23).

During the sintering (step 7, 21), it is possible to adjust the partial pressure of oxygen p_{O2}, preferably by humidification, in order to improve the interdiffusion of the PuO_2 and UO_2 oxides.

The main types of scrap encountered in the art are summarized below, by way of example.

Form	*Origin*	*Characteristics before treatment*	*% scrap (in mass of PuO_2)*
Powders	End of pellet-pelletizing batch	Unsintered powder with uncontrolled particle size distribution and sinterability	99.5%
	Grinding powders	Sintered powder with uncontrolled particle size distribution and sinterability	
	Recovery of dust	Uncontrolled PuO_2 and impurity content and particle size distribution	
Pellets	Rejects from sorting by aspect	Sintered pellets	
	Samples		
	Excess production		
Various	Chemical analyses	Nitric solutions	0.5%
	Maintenance and cleaning of production equipment and/or gloveboxes	Volatile chemical impurities	
		Nonvolatile chemical impurities	

The steps of crushing (step 22) (optional) and of micronization (step 23) the pellets can be turned to advantage also for recycling scrapped pellets, for example on sorting (step 9), and for increasing the size of the batches of scrap powder homogenized and characterized before recycling.

It must be understood that the present invention is in no way limited to the embodiments described above and that many modifications may be carried out thereon without departing from the scope of the claims given below.

For laboratory nitric solutions, it is possible to use precipitation and calcination before dry recycling as for the scrap mentioned above.

For scrap which exceptionally has excess nonvolatile chemical impurities, it is possible to use, for example, chemical pretreatment in an aqueous phase.

The process of recycling scrap according to the invention can also be turned to advantage in order to recycle, as raw materials, unirradiated pellets of $(U,Pu)O_2$ mixed-oxide nuclear fuel, possibly produced by different processes (for example, originating from the scrap of unirradiated mixed oxide fuels and intended for advanced reactors or research reactors).